# CXCVI.—*Complex Formation amongst the Nitrates. Part II. The Ternary System Phenol–Silver Nitrate–Water.*

By Charles Reynolds Bailey.

Silver nitrate, owing to its low melting point and small heat of fusion, has a high solubility in many solvents of diverse types. Müller, Raschka, and Wittmann (*Monatsh.*, 1927, **48**, 659) report, for example, that at 25°, 100 c.c. of acetonitrile and of ethylene glycol respectively dissolve 87·6 and 53·9 g. of this salt. Basic substances such as the amines are also usually good solvents, but monohydric alcohols, esters, ketones, and organic acids are poor: within an homologous series, a higher dielectric constant is generally accompanied by an increase in solvent power for silver nitrate, although this effect may sometimes be offset by an increase in molecular weight, such as is involved in piling up a heavy nucleus.

The foregoing remarks are illustrated in Table I by solubility data taken chiefly from the work of Müller (*Z. anorg. Chem.*, 1925, **142**, 130), and from Müller, Raschka, and Wittmann (*loc. cit.*). The solubility ($s$) is given in g. per 100 c.c. of solvent of dielectric constant, $D$, at the temperature $T$°. Succinonitrile has a dielectric constant of 66 and silver nitrate has a correspondingly high solubility in this solvent; it is not possible to give a definite value, however, for the solid phase at the temperatures under consideration is a compound of solvent and solute. The present

TABLE I.

| Solvent. | *T.* | *D.* | *s.* |
|---|---|---|---|
| Methyl alcohol | 20° | 31·2 | 2·84 |
| Ethyl alcohol | 20 | 26·8 | 1·67 |
| Ethylene glycol | 25 | 41·2 | 53·9 |
| Methyl ethyl ketone | 25 | 17·8 | 0·17 |
| Acetophenone | 25 | 15·8 | 0·007 |
| Aniline | 20 | 7·2 | 18·5 |
| Dimethylaniline | 20 | 5·1 | insol. |
| Acetonitrile | 20 | 35·8 | 87·6 |
| Acetic acid | 25 | 6·4 | insol. |

work shows that, although phenol has a low dielectric constant (9·7), nevertheless it is an extremely good solvent, 100 c.c. at 25° dissolving some 82 g. of silver nitrate.

The conductivities of many of the above solutions have been measured and are in some cases greater than in the aqueous solution of corresponding dilution (Dutoit and Friedrich, *Bull. Soc. chim.*, 1898, **19**, 321). From the results of potentiometric measurements, the existence of complexes between the solute and solvent molecules has been deduced; for instance, Bodländer (*Z. anorg. Chem.*, 1904, **39**, 204) and, in particular, Pawelka (*Z. Elektrochem.*, 1924, **30**, 180) have examined a number of such solutions, the latter postulating a general formula, $Ag_mR_n(NO_3)_m$, where $m = 1$ and $n = 2$ in most cases. The existence of a complex ion of this type was further confirmed by Schmidt and Keller (*Z. physikal. Chem.*, 1929, *A*, **141**, 331), who attempted, by means of cryoscopic and conductivity measurements, to estimate the number of water and alcohol molecules associated with the silver ion. They showed that both pyridine and ammonia, added to such solutions, gave rise to a complex ion of the type $AgX_2^{\bullet}$.

In a series of papers, Endo recorded the activity of phenol in various aqueous salt solutions (*Bull. Chem. Soc. Japan*, 1926, **1**, 25; 1927, **2**, 124, 147) as found from the depression of freezing point of these solutions both in the absence and in the presence of phenol; he showed that normally the activity of phenol and the depression of freezing point due to it increase when a salt is added, but that silver nitrate forms an exception to this rule, for it " salts in " phenol in aqueous solution. He attributed the phenomenon to the formation of a complex ion $[Ag,C_6H_6O]^{\bullet}$, and stated that the solution of silver nitrate in phenol was colourless and gave no sign of compound formation.

The extremely high solubility suggests compound formation, and it was decided to examine this binary system further, and also to investigate the ternary equilibria in the aqueous solution. In a number of cases, definite compounds of silver nitrate with the solvent had already been isolated; with pyridine, three are known

(Kahlenberg and Brewer, *J. Physical Chem.*, 1908, **12**, 283; Jörgensen, *J. pr. Chem.*, 1886, **33**, 501), containing one molecule of silver nitrate to 6, 3, and 2 molecules of solvent, whilst succinonitrile, on the other hand, gives compounds in which one molecule of the solvent is united with 4, 2, and 1 molecules of the solute (Middelberg, *Z. physikal. Chem.*, 1903, **43**, 305). Similar compounds are known with the halogen derivatives of the nitriles (Scholl and Steinhoff, *Ber.*, 1906, **39**, 4393).

## EXPERIMENTAL.

*The Binary Systems.*—(1) *Phenol–water.* Detached crystals of absolute phenol were twice distilled, the initial and final fractions being rejected; the product had m. p. 40·8° (uncorr.). The equilibria in the binary system have already been fully discussed (see, *e.g.*, Rhodes and Markley, *J. Physical Chem.*, 1921, **25**, 527; Bailey, J., 1925, **127**, 1951; Hill and Malisoff, *J. Amer. Chem. Soc.*, 1926, **48**, 918; Wilcox and Bailey, *J. Physical Chem.*, 1929, **33**, 705).

(2) *Silver nitrate–water.* The solubility of silver nitrate in water has been determined by a number of observers, the agreement being poor (see Landolt–Börnstein, " Tabellen," 5th edtn., I, 635 for references; also Kazantzev, *Trans. Inst. Chem. Reagents, Moscow*, 1923, **2**, 10). In this and the ternary system, silver nitrate was estimated by standard potassium or sodium chloride solution prepared from the fused A.R. salt, identical results being obtained by the use of either standard. Equilibrium was approached from both sides. Table II gives the equilibria in the system below 40°, the results being reasonably in accordance with the means of published data.

TABLE II.

| Temp. | Solid phase. | $AgNO_3$, %. | Temp. | Solid phase. | $AgNO_3$, %. |
|---|---|---|---|---|---|
| 0·0° | Ice | 0·0 | 20·0° | $AgNO_3$ | 68·6 |
| −5·6 | ,, | 34·2* | 25·0 | ,, | 71·0 |
| −7·3 | Ice + $AgNO_3$ | 47·1† | 30·0 | ,, | 73·2 |
| 10·0 | $AgNO_3$ | 61·8 | 35·0 | ,, | 75·4 |

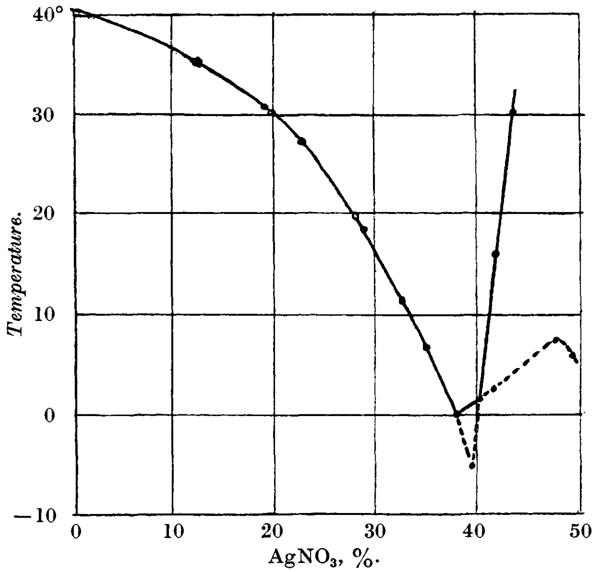
* Rüdorff, *Annalen*, 1872, **145**, 600. † Middelberg, *loc. cit.*

(3) *Silver nitrate–phenol.* The system was partly explored by thermal methods, certain of the points near room temperature being checked by quantitative determination of the silver nitrate. Reduction of the nitrate was avoided by powdering and warming the salt and then dissolving it in the heated solvent; strong heating or very long standing caused considerable decomposition, and it was not possible to examine solutions containing more than 50% of nitrate. Fig. 1 and Table III represent the experimental results.

It will be seen that a *compound* $AgNO_3,2C_6H_5\cdot OH$ has been definitely isolated, although its limits of stable existence are narrow; it crystallises in white cubes and has a metastable m. p. at 7·6°; it was necessary to supercool to the region of — 30° before the compound was first obtained. It is noteworthy in this connexion that Krause and Schmitz (*Ber.*, 1919, **52**, 2150) isolated a silver phenyl silver nitrate of similar formula, $AgNO_3,2PhAg$. The initial depression of the freezing point of phenol by addition of silver nitrate gives a calculated molecular weight of the order of 200; in aqueous solution the behaviour of this salt is somewhat similar, but the effect is due to association of the anion in the more concentrated solutions (compare Sidgwick, " Electronic Theory of Valency," 1927, p. 195). Sidgwick and Ewbank (J., 1924, **125**, 2273) have shown, however, that, whilst salts may be divided sharply into two classes according as they form solid hydrates or not, the former class as a whole gives a greater depression of the freezing point of water than the latter, among which silver nitrate should occur. It seems that in the case of the phenolic solution of silver nitrate, we have, on the evidence available, to attribute the large depression of freezing point to the removal of the solvent from the system by solvation, as in the case of those salts which form hydrates.

FIG. 1.

*The system silver nitrate–phenol.*



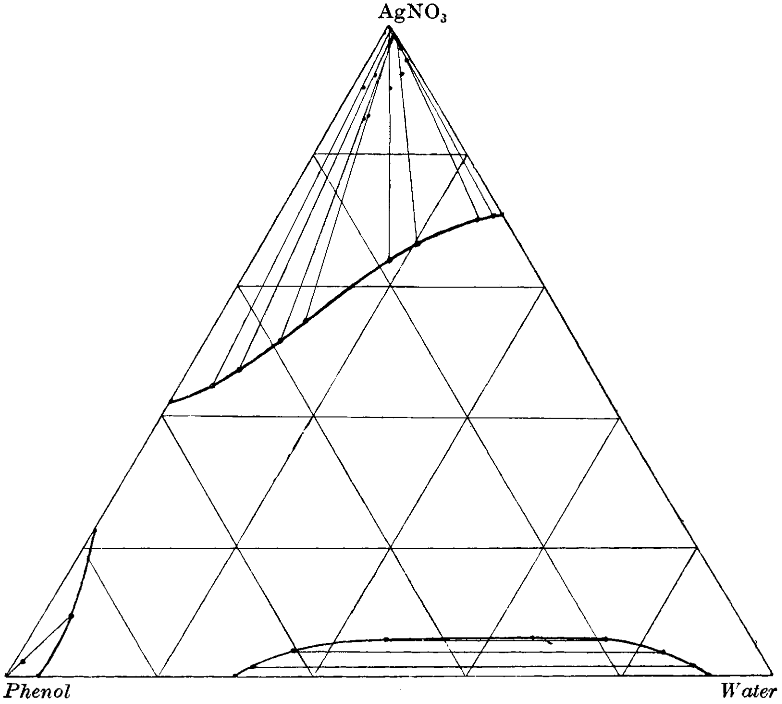
### TABLE III.

| Temp. | Solid phase. | $AgNO_3$, %. | Temp. | Solid phase. | $AgNO_3$, %. |
|---|---|---|---|---|---|
| 35·5° | Phenol | 11·9 | 16·0° | $AgNO_3$ | 41·5 |
| 27·2 | ,, | 22·1 | 30·2 | ,, | 43·2 |
| 11·4 | ,, | 31·8 | | Metastable. | |
| 0·0 | $C_6H_6O$ + compound | 37·5 | −5·3 | Phenol + $AgNO_3$ | 39·0 |
| 1·4 | Compound + $AgNO_3$ | 39·8 | +7·6 | Compound (m. p.) | 47·4* |

* $AgNO_3,2C_6H_6O$ requires $AgNO_3$, 47·5%.

FIG. 2.

*The ternary system silver nitrate–phenol–water at 25°.*



*The Ternary System.*—The solutions were sucked through a filter into a weighing bottle and analysed, together with the moist residue, phenol being estimated by the bromide–bromate method. A number of interesting phenomena were noticed during the exploration of the isotherm at 25°. Solutions containing more than 30% of phenol with silver nitrate as the solid phase were extremely viscous. Again, no difficulty was experienced in separating the two liquid layers in the binodal curve: normally phenol and water mixtures separate, on cooling or after shaking, with the formation of a persistent emulsion, 2 or 3 days being sometimes required for complete clearance; it was found that the addition of even a trace of silver nitrate reduced this time to the order of 1 minute, in powerful contrast to the action of most other substances that "salt in" phenol, such as the oleates, which produce very stable emulsions. The molecular elevation of critical solution temperature is given by $E = (t - T)/C$, where $t - T$ is the elevation in degrees and $C$ is the concentration of added salt in mols. per kg. of phenol–water mixture. At the critical composition (36·5% of phenol), $T = 65{\cdot}3°$, and if $t$ is taken as 25°, $E$ is of the order of $-100°$, *i.e.*, much the same as for other substances of diverse types, pyrogallol and succinic acid giving a value of $-90°$. The soaps are anomalous, sodium oleate having $E = -680°$ (Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129; Bailey, J., 1923, **123**, 2579). The system was explored at 25°, and no compounds or mixed crystals were found at this temperature. The equilibria are illustrated in Table IV and Fig. 2.

TABLE IV.

*Ternary system phenol–water–silver nitrate at* 25°.

Percentages by weight.

| | | Solution. | | | Residue. | | | |
|---|---|---|---|---|---|---|---|---|
| No. | $d^{25°}_{25°}$. | $AgNO_3$. | $C_6H_6O$. | Water. | $AgNO_3$. | $C_6H_6O$. | Water. | Phases present. |
| 1 | 2·317 | 71·0 | — | 29·0 | — | — | — | $AgNO_3$ + soln. |
| 2 | 2·297 | 70·8 | 1·1 | 28·1 | 96·1 | 0·4 | 3·5 | |
| 3 | 2·283 | 69·9 | 3·9 | 26·2 | 94·7 | 0·5 | 4·8 | |
| 4 | 2·170 | 66·0 | 13·6 | 20·4 | 92·2 | 2·7 | 5·1 | |
| 5 | 2·093 | 63·4 | 18·6 | 18·0 | 90·0 | 5·0 | 5·0 | |
| 6 | 1·878 | 54·1 | 34·1 | 11·8 | 85·9 | 10·0 | 4·1 | |
| 7 | 1·812 | 51·4 | 39·0 | 9·6 | 85·3 | 10·7 | 4·0 | |
| 8 | 1·736 | 47·0 | 46·2 | 6·8 | 92·2 | 5·8 | 2·0 | |
| 9 | 1·688 | 44·6 | 50·9 | 4·5 | 89·7 | 8·5 | 1·8 | |
| 10 | 1·633 | 42·4 | 57·6 | — | — | — | — | |
| 11 | — | 9·3 | 86·6 | 4·1 | 2·6 | 96·2 | 1·2 | $C_6H_6O$ + soln. |
| 12 | — | 24·0 | 76·0 | — | — | — | — | |
| 13 | — | — | 95·7 | 4·3 | — | — | — | |
| 14 | — | 1·4 | 9·6 | 89·0 | 1·1 | 66·9 | 31·9 | Two liquids. |
| 15 | — | 3·4 | 12·8 | 83·8 | 3·5 | 60·6 | 35·9 | |
| 16 | — | 5·3 | 19·0 | 75·7 | 5·6 | 47·8 | 46·6 | |
| 17 | — | 6·0 | 31·0 | 63·0 | (Critical point) | | | |

The distribution ratio of silver nitrate between the phenolic and the aqueous layer for points 14, 15, and 16 (calculated as g. of salt per 100 g. of phenol–water mixture) is 0·79, 1·03, and 1·06 respectively.

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